Combinatorial Adhesion Measurements: Factorial Design Concepts for Data Collection and Library Evaluation

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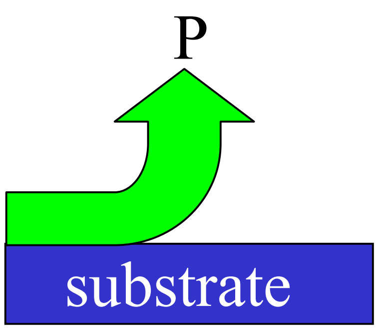
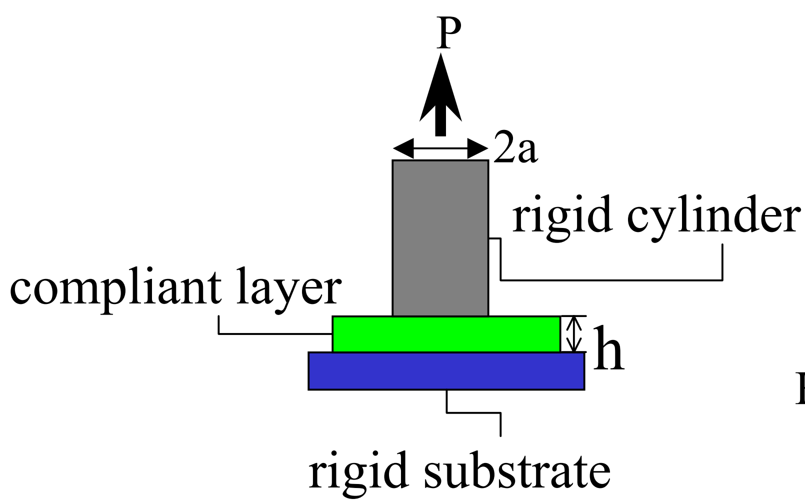
Adhesion Testing

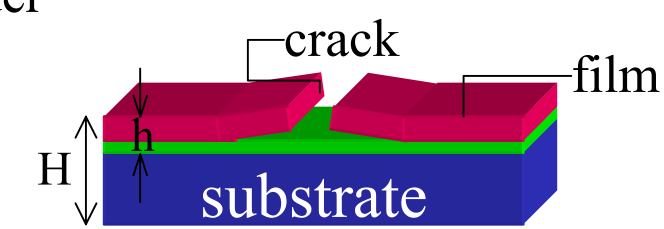
- Adhesion is critical to the performance of many industrial and household products.
- It involves a complex interplay between the adhesive and substrate that involves an understanding of *surface properties*, *adhesive structure-property relationships, and surface forces*.



Peel Test



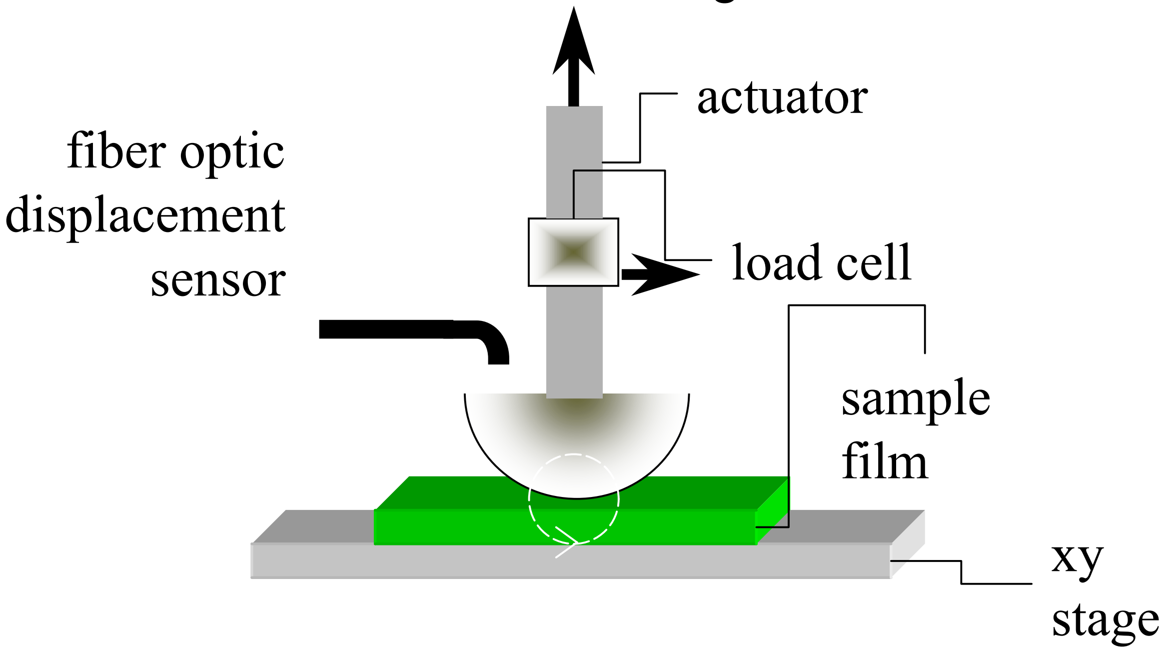
Punch Test



Mixed Mode Flexure Test

Axisymmetric Adhesion Tests

Theory of Johnson, Kendall, and Roberts quantifies the surface energy and work of adhesion by relating the load required to hold an equilibrium contact area between two contacting materials.

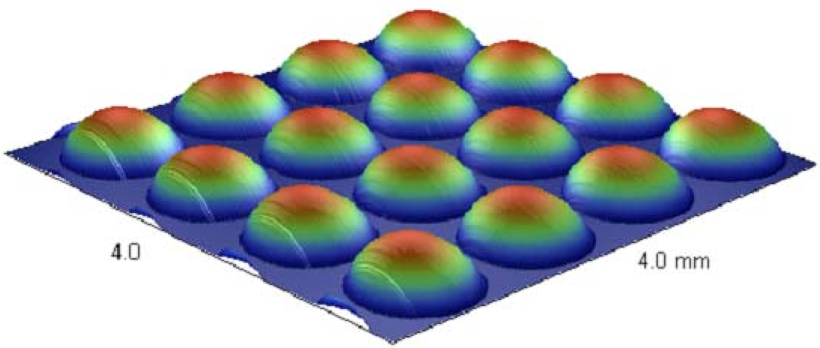


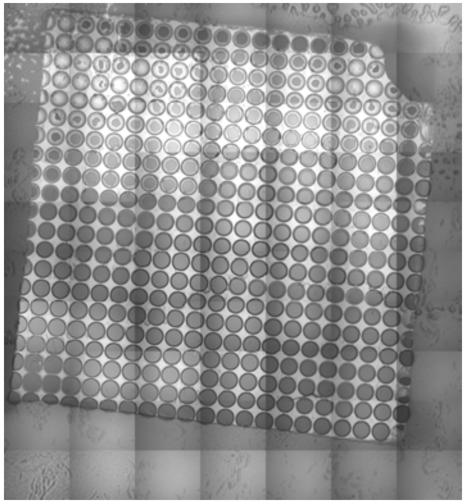
$$a^3 = \frac{3R}{4E^*}\left[P + 3\pi GR + \sqrt{6GRP + (3\pi GR)^2}\right]$$

JKR Equation

Axisymmetric Adhesion Tests

- NIST is currently developing a Multi-lens Combinatorial Adhesion Test (MCAT)
  - The goal is to measure adhesion across gradient libraries in a high-throughput fashion.

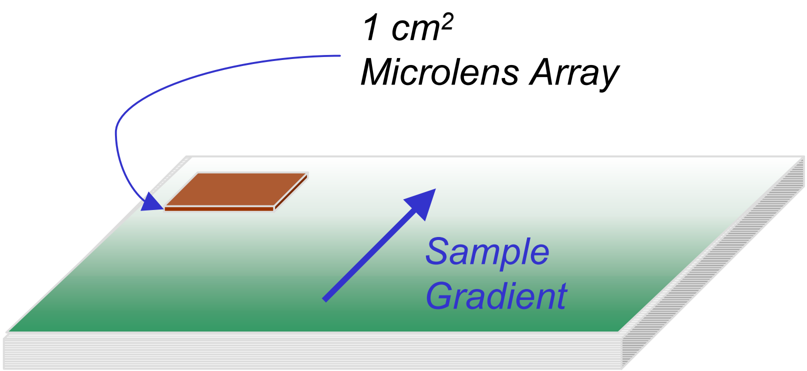




- Array of 324 larger lenses covering 3.25 cm^2
- 900 μm diameter, 300 um high

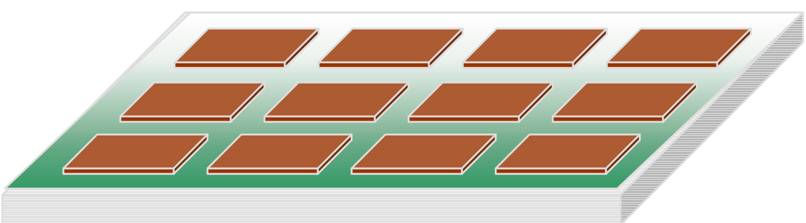
- Array of 1600 larger lenses covering 1 cm^2
- 250 μm diameter, 22 um high

Data Analysis and Storage



3 cm x 5 cm gradient library

Single Microlens Test



Multiple tests with a Microlens Array

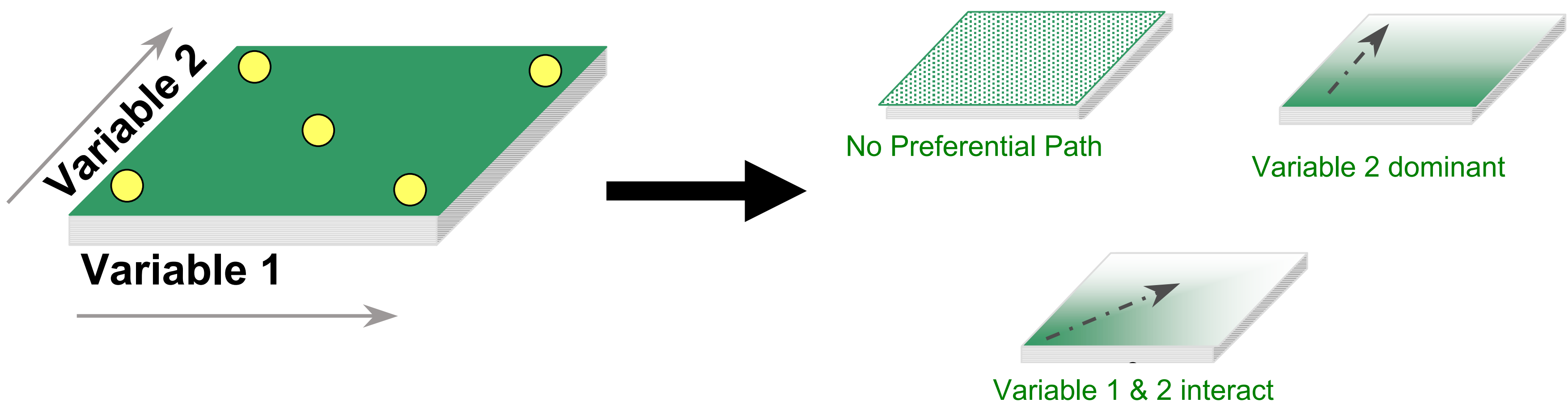
Multiple Microlens Test

- Typical data generation
  - 50 pictures
  - 67 Megabytes
  - Fit displacement and area data for 6 lenses

- Workload increases by a factor of n=12.
  - 600 pictures
  - 804 Megabytes
  - Fit displacement and area data for 72 lenses

Can Design of Experiments reduce the increased workload?

Design of Experiments



Adhesion is measured across the sample in a few areas (yellow spots).

A representative surface map is created by following the *Preferential Testing Path.*

- The design of experiments approach reduces the number of experiments through statistical evaluation of the gradient library to determine the most efficient testing path.

Axisymmetric Adhesion Tests

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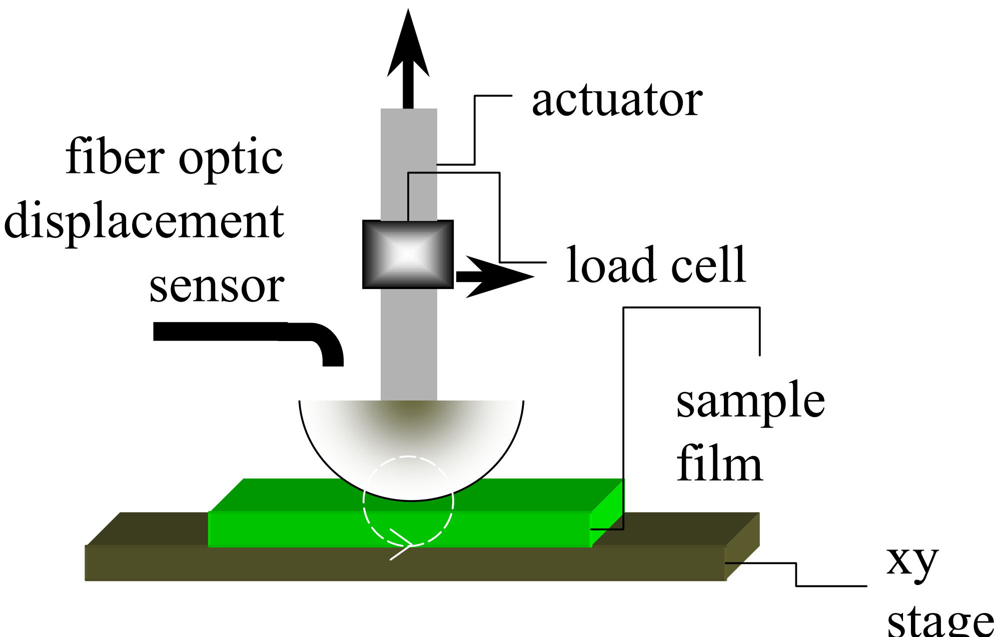
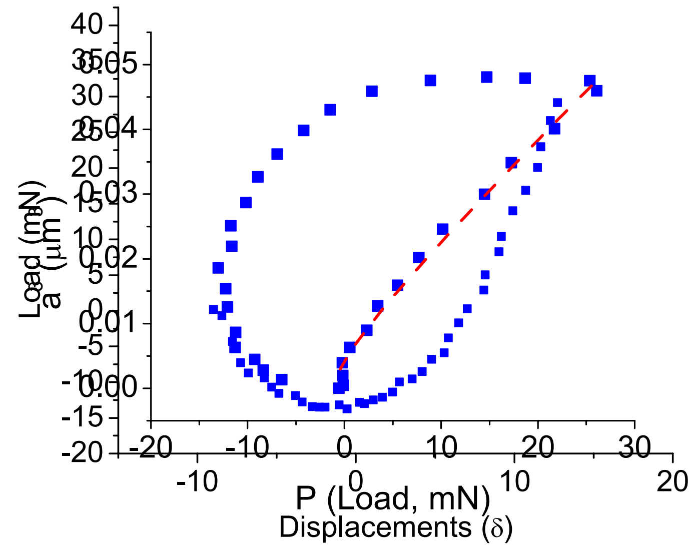




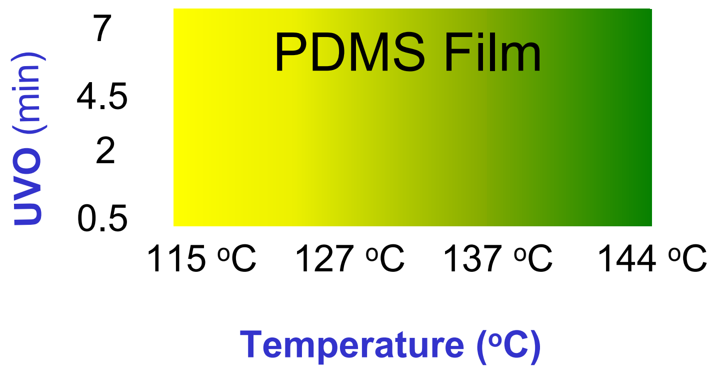
$$a^3 = \frac{3R}{4E^*}\left[P + 3\pi GR + \sqrt{6GRP + (3\pi GR)^2}\right]$$

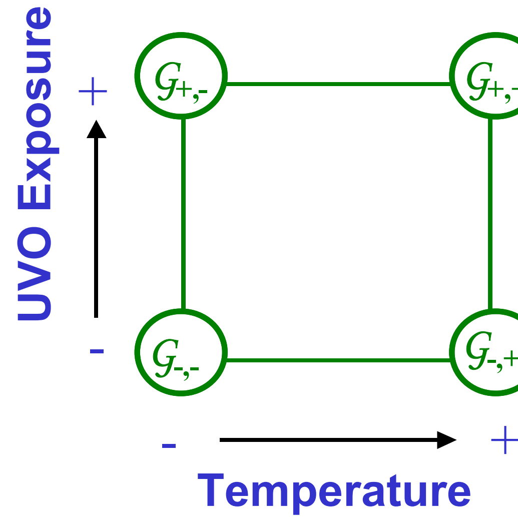
JKR Equation

PDMS-Glass Adhesion

- **Materials**
  - Polydimethylsiloxane (PDMS) film
    - DOW Sylgard 184 mixed in a ratio of 15:1 prepolymer to catalyst. [Need a better description]
  - Film initially cured on a **115 - 144 °C** temperature gradient.
  - Film exposed to a gradient in UV-ozone exposure time orthogonal to the temperature gradient, **30 sec – 7 min**.
- **Measurements**
  - Measure adhesion at the gradient “extremes” and evaluate each treatments *effect* on adhesion.
  - Measure adhesion across entire film in a grid fashion.
    - Single glass hemispherical indenter, R=4.935 mm
    - Loading/unloading velocity of 500 nm/s
    - Indenter displacements ~15 μm and no dwell time
    - Experiment turn around is under 8 hours.

Factorial Design at Two Levels





$$\boxed{\text{main T effect} = \overline{\mathrm{G}}_{T+} - \overline{\mathrm{G}}_{T-}}$$

$$\boxed{\text{main UV effect} = \overline{\mathrm{G}}_{\mathrm{U}V+} - \overline{\mathrm{G}}_{\mathrm{U}V-}}$$

$$\boxed{\text{T x UV interaction} = \frac{1}{2}\left(\overline{\mathrm{G}}_{T+} - \overline{\mathrm{G}}_{T-}\Big|_{\mathrm{U}V+} - \overline{\mathrm{G}}_{T+} - \overline{\mathrm{G}}_{T-}\Big|_{\mathrm{U}V-} \right)}$$

Main Effects for Adhesion and Tack

Unexposed PDMS film

	E (Mpa)	*$\mathcal{G}$ (J/m^2)*	*W' (J/m2)*
T+	3.14	0.0434	0.544
T-	2.20	0.0350	0.374
Effect	**0.94**	0.008	**0.170**

- Error associated with each measurement:
  - **E = ± 0.15 MPa**
  - **G = ± 0.02 J/m^2**
  - **W' = ± 0.01 J/m^2**

- Curing temperature affects both system modulus and the unloading work of adhesion.

- The work of adhesion from loading curves appears unaffected by curing temperature.

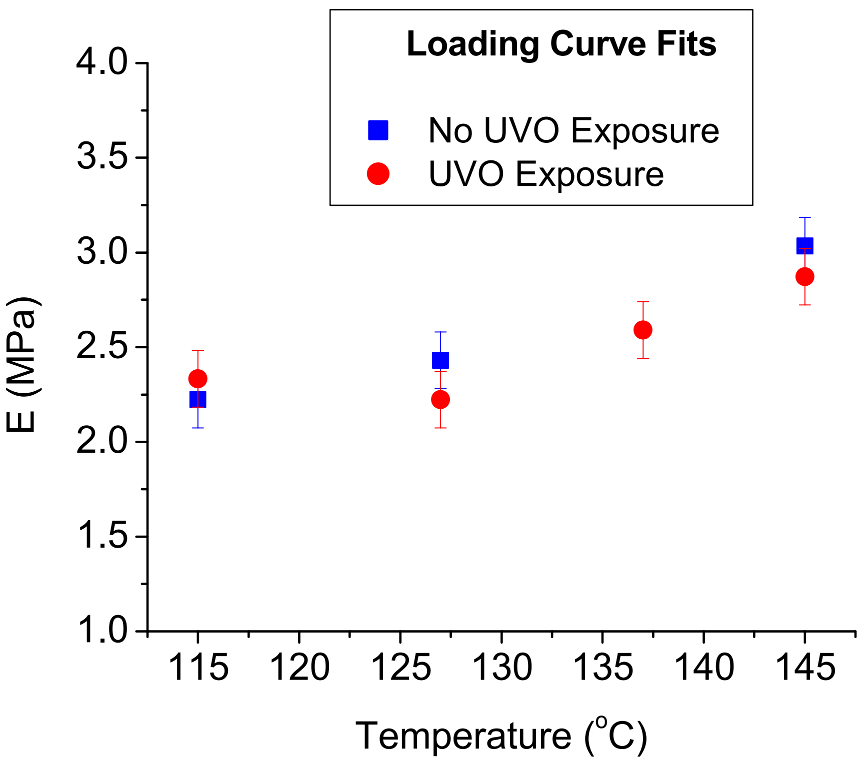
Exposed PDMS film

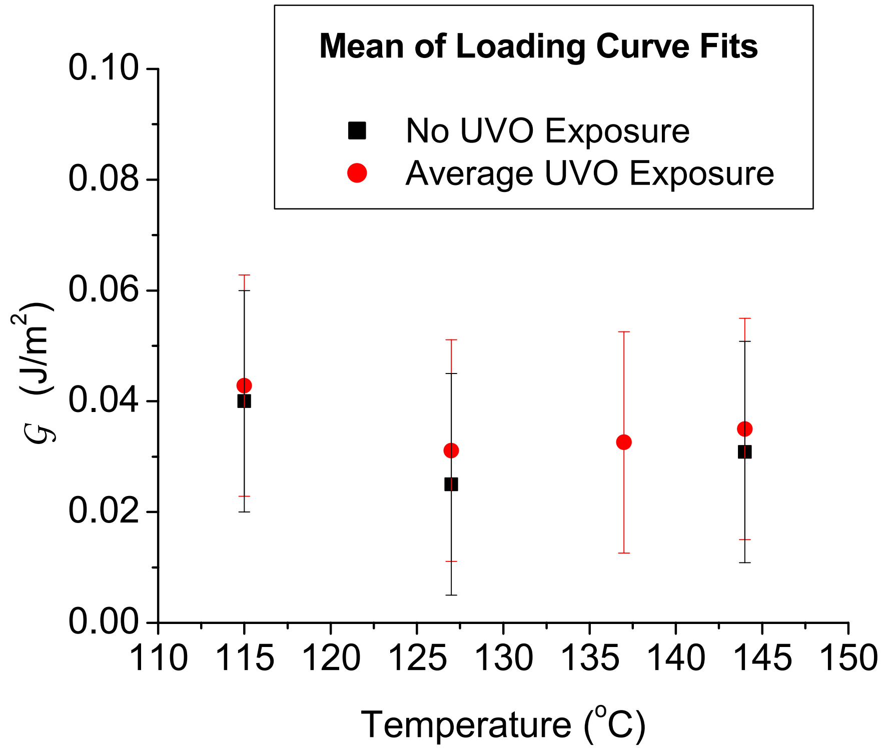
	E (Mpa)	*$\mathcal{G}$ (J/m^2)*	*W' (J/m2)*
T+	2.93	0.0350	0.620
T-	2.32	0.0445	0.488
Effect	**0.62**	-0.009	**0.413**

	E (Mpa)	*$\mathcal{G}$ (J/m^2)*	*W' (J/m2)*
UVO+	2.79	0.0447	0.572
UVO-	2.46	0.0302	0.413
Effect	**0.33**	0.015	**0.159**

- The effect of curing temperature on system modulus is still observed after UVO exposure.
- The work of adhesion from unloading is affected by UVO exposure.
- There does not appear to be a large effect of UVO on loading work of adhesion.

JKR Parameters

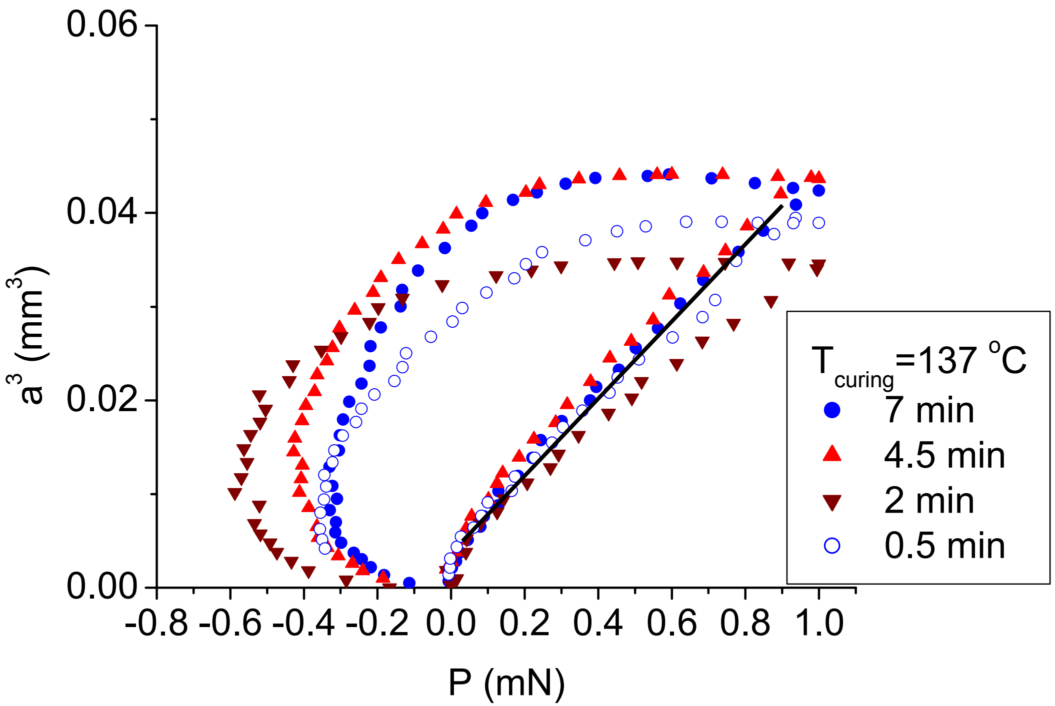




- The modulus increases with curing temperature

- The work of adhesion remains relatively constant across the temperature gradient.

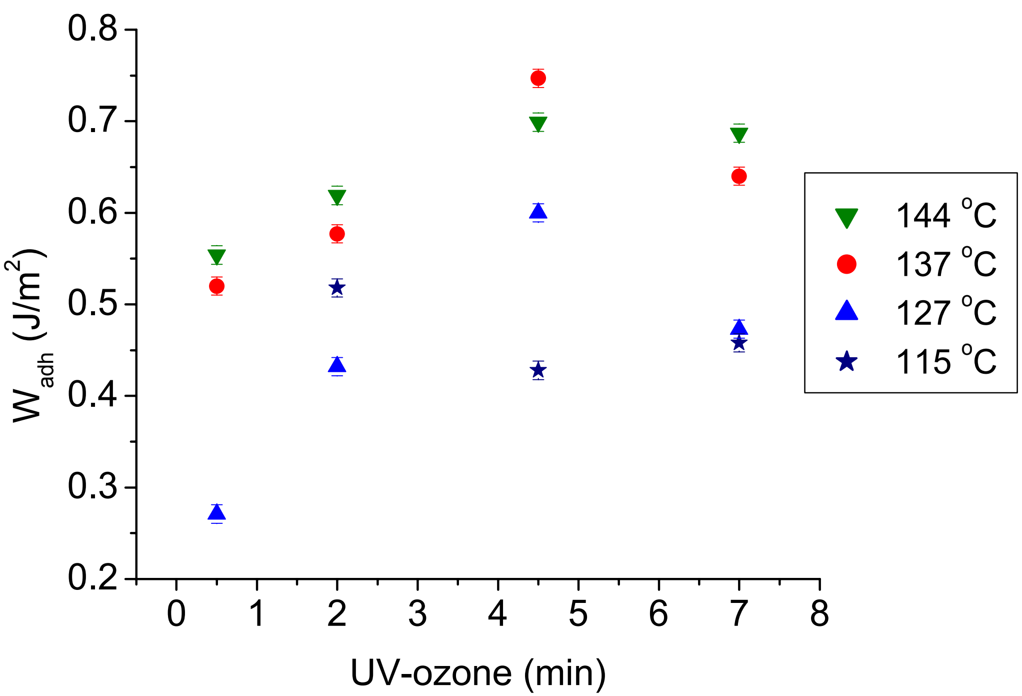
Adhesion Hysteresis

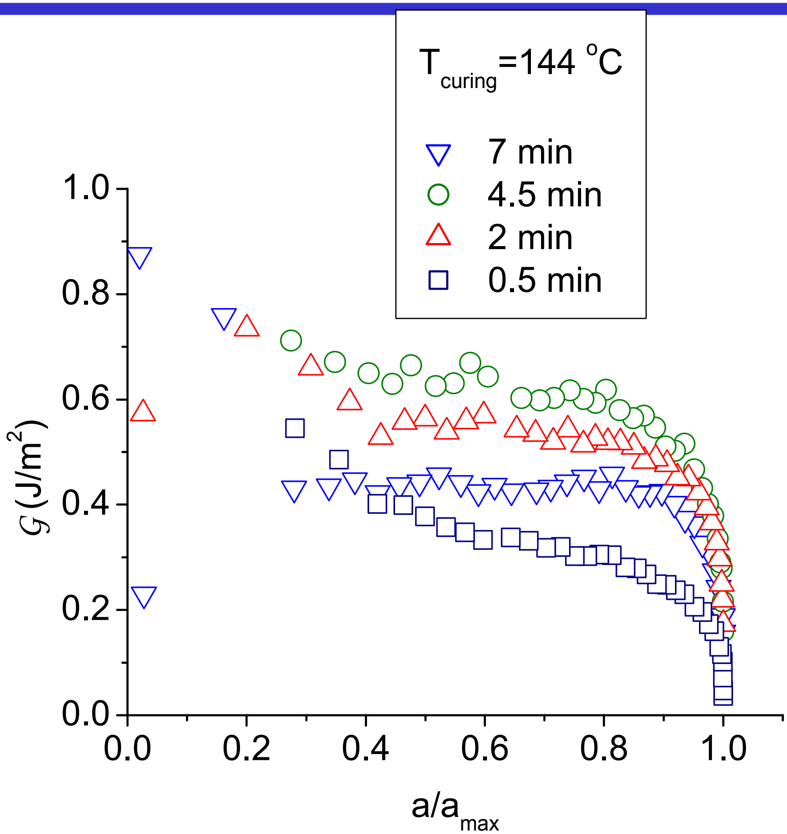


- The increase in UVO exposure at constant curing temperature increases the adhesion hysteresis.
- Loading curve fit to 7 min exposure data with the JKR equation:
  - **$\mathcal{G}$ = 0.030 J/m²**
  - **E = 2.322 MPa**
  - **R = 4.935 mm**

$$a^3 = \frac{3R}{4E^*}\left[P + 3\pi GR + \sqrt{6GRP + (3\pi GR)^2}\right]$$

Work of Adhesion during Unloading



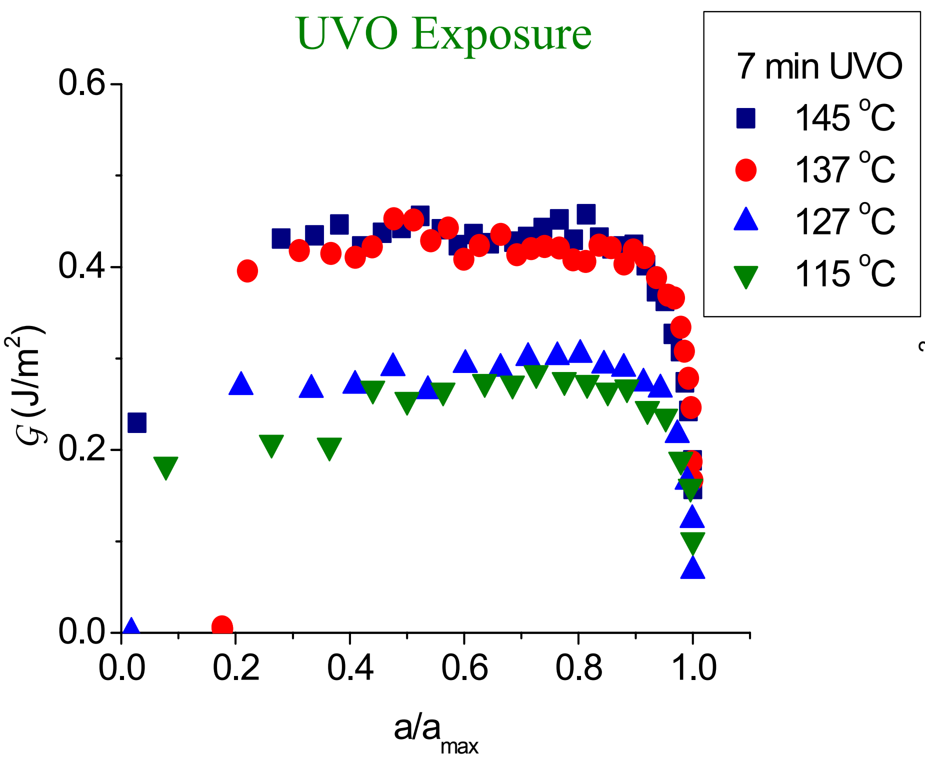


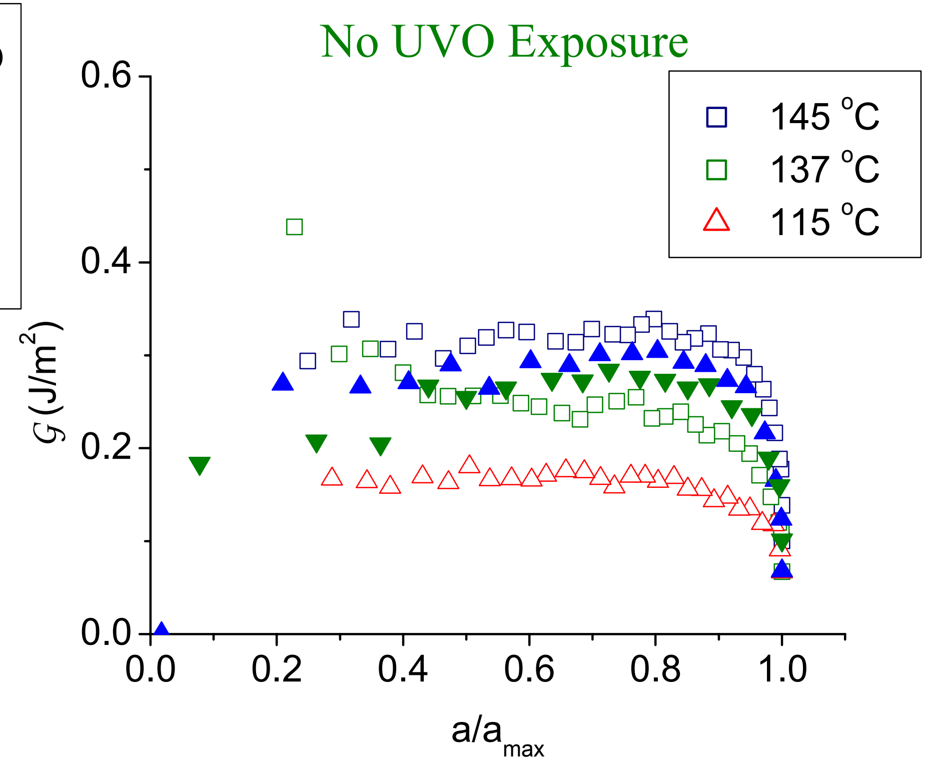
$$W^*_{adh} = \frac{\int_{\delta_{max}}^{\delta_{final}} P d\delta}{\pi a_{max}^2}$$

$$G = \frac{3(P' - P)^2}{32 \pi E a^3}$$

*Crosby, A. J.; Shull, K. R.; *J. Poly. Sci. B* (**1999**), 37, 3455-3472.

Surface Reorganization?





- At the higher curing temperatures, it takes more energy to start the movement of the crack than at lower temperatures.
- The lower temperatures appear to shift towards the untreated values at the higher temperatures.

Conclusions

- **Design of Experiments** can be used to increase adhesion measurement efficiency across gradient samples. It can be sensitive to outliers.
- Curing the PDMS film on a temperature gradient stage results in a gradient system modulus across the film for short times. This gradient was found to be unaffected by UVO exposure.
- Increasing the UVO exposure increases the tackiness of the PDMS film. This increase in tackiness appears to decrease with time.

Acknowledgements

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